The suitability of ^{236}U as an ocean tracer

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^{236}U is probably the second most abundant anthropogenic radionuclide (above 10^6 kg produced so far [1]). While previous measurements could identify ^{236}U only in the vicinity of known contaminated sites (Chernobyl, Sellafield, etc.), our measurements are evolving into a consistent picture of the dispersion of anthropogenic ^{236}U. This led to the insight that ^{236}U is a component of the global fallout from nuclaer weapons testing and was produced via the $^{238}U(n, 3n)^{236}U$ reaction [2].

^{236}U has a well defined source function, is conservative in sea water (residence time approximately 500000 years) and has a sufficiently long half-life (23 Ma) to assure complete mixing in the ocean. The expected natural level below 10^{-13} is negligible compared to the measured anthropogenic ratios. ^{236}U is thus suitable as a tracer for the study of ocean dynamics on a global scale and may in some respects even outperform some more established isotopes.

We analyzed sea water samples from places around the world: the Atlantic ocean ($^{236}U/U = (1.9\pm0.6)\times10^{-9}$), the Pacific ocean ($^{236}U/U = (5.2\pm0.5)\times10^{-9}$), the Black Sea ($^{236}U/U = (3.6\pm0.5)\times10^{-9}$) and the Irish Sea ($^{236}U/U = (2.0\pm0.02)\times10^{-6}$). The measured isotopic ratios coincide with established values for contamination by global fallout, except from Irish Sea water, which was clearly influenced by the Sellafield reprocessing plant.

[1] Steier (2008) *Nucl. Instr. and Meth.* B **266** 2246-2250. [2] Sakaguchi (2009) *Science of the Total Environment* **407** 4238-4242.

An absolute reference frame for clumped isotope thermometry

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Analysis of multiply substituted isotopologues of molecules (‘clumped isotope geochemistry’) presents special challenges to both precision and accuracy. Previous discussions have focused on mass spectrometric precision for these rare species and intralaboratory reference frames. This discipline has spread, demanding interlaboratory standardization. We present a four-laboratory study of the calibration of mass-47 anomalies (Δ_{47} values) in CO_2 (especially extracted from carbonate). We consider: instrument linearity, source fragmentation/recombination reactions (which vary between mass spectrometers and with time and instrument settings), and differences in methods, materials and conditions for sample preparation. We address these problems by developing a method for standardizing Δ_{47} measurements to an absolute reference frame based on theoretical predictions of the abundances of multiply-substituted isotopologues of gaseous CO_2 that has reached a thermodynamic equilibrium at a known temperature. By analyzing CO_2 gases that have been subjected to established laboratory procedures known to promote isotopic equilibration (i.e., heated gases and water-equilibrated CO_2), and by reference to the statistical thermodynamic predictions of equilibrium isotopic distributions, it is possible to construct an empirical transfer function that can then be applied to CO_2 samples with unknown Δ_{47} values. This reference frame may be unique in that it is based on thermodynamic equilibrium, rather than the isotopic composition of an arbitrary reference material. We describe the protocol necessary to construct such a reference frame, the method for converting gases with unknown clumped isotope compositions to this frame, and suggest a protocol for ensuring that reported Δ_{47} values can be compared among different laboratories, independent of laboratory-specific analytical or methodological artefacts. Application of this approach to measurements of CO_2 extracted from several carbonate reference materials results in interlaboratory agreement on their Δ_{47} values to within est. ±0.01 ‰, 1σ. Finally, we present a revised paleotemperature scale that applies when using the absolute reference frame described here, as opposed to the previous paleotemperature equation based on data from a single laboratory. More generally, this study presents a model for how interlaboratory standardization might be approached for other ‘clumped isotope’ measurements.